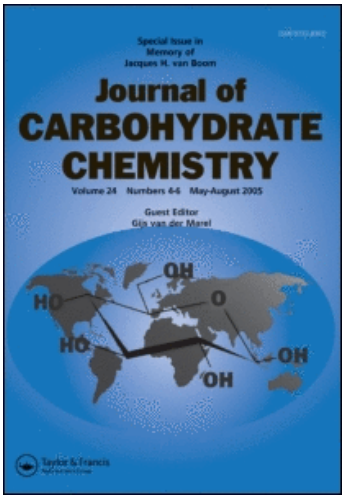


## Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

# Syntheses of Pseudo-α-D-Glucopyranose and Pseudo-β-L-Altropyranose From L-Arabinose

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**To cite this Article** Tadano, Kin-Ichi , Kameda, Yuklaki , Limura, Youichi and Suami, Tetsuo(1987) 'Syntheses of Pseudo-α-D-Glucopyranose and Pseudo-β-L-Altropyranose From L-Arabinose', Journal of Carbohydrate Chemistry, 6: 2, 231 — 244
**To link to this Article: DOI:** 10.1080/07328308708058873
**URL:** http://dx.doi.org/10.1080/07328308708058873

J. CARBOHYDRATE CHEMISTRY, 6(2), 231-244 (1987)

# SYNTHESES OF PSEUDO-α-D-GLUCOPYRANOSE AND PSEUDO-β-L-ALTROPYRANOSE FROM L-ARABINOSE

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Received September 24, 1986 - Final Form November 8, 1986



## ABSTRACT

Two optically active pseudo-hexopyranoses, pesudo-α-D-glucopyranose (1) and pseudo-β-L-altropyranose (2), were synthesized starting from L-arabinose. L-Arabinose was first converted to an acyclic aldehyde 9. The reaction of 9 with dimethyl malonate under basic conditions provided a tetrahydroxylated cyclohexane-1,1-dicarboxylate 11 and a C-glycoside of β-L-arabinopyranose 12. From the compound 11, the desired two pseudo-sugars were synthesized by 1) thermal demethoxycarbonylation, 2) $LiAlH_4$ reduction, 3) hydroboration of the resulting 1-hydroxymethyl-1-cyclohexene 14 followed by hydrogen peroxide treatment, and 4) removal of the protecting groups.

## INTRODUCTION

2,3,4,5-Tetrahydroxy-1-(hydroxymethyl)cyclohexanes, often designated as the "pseudo-sugars", are known to be components of

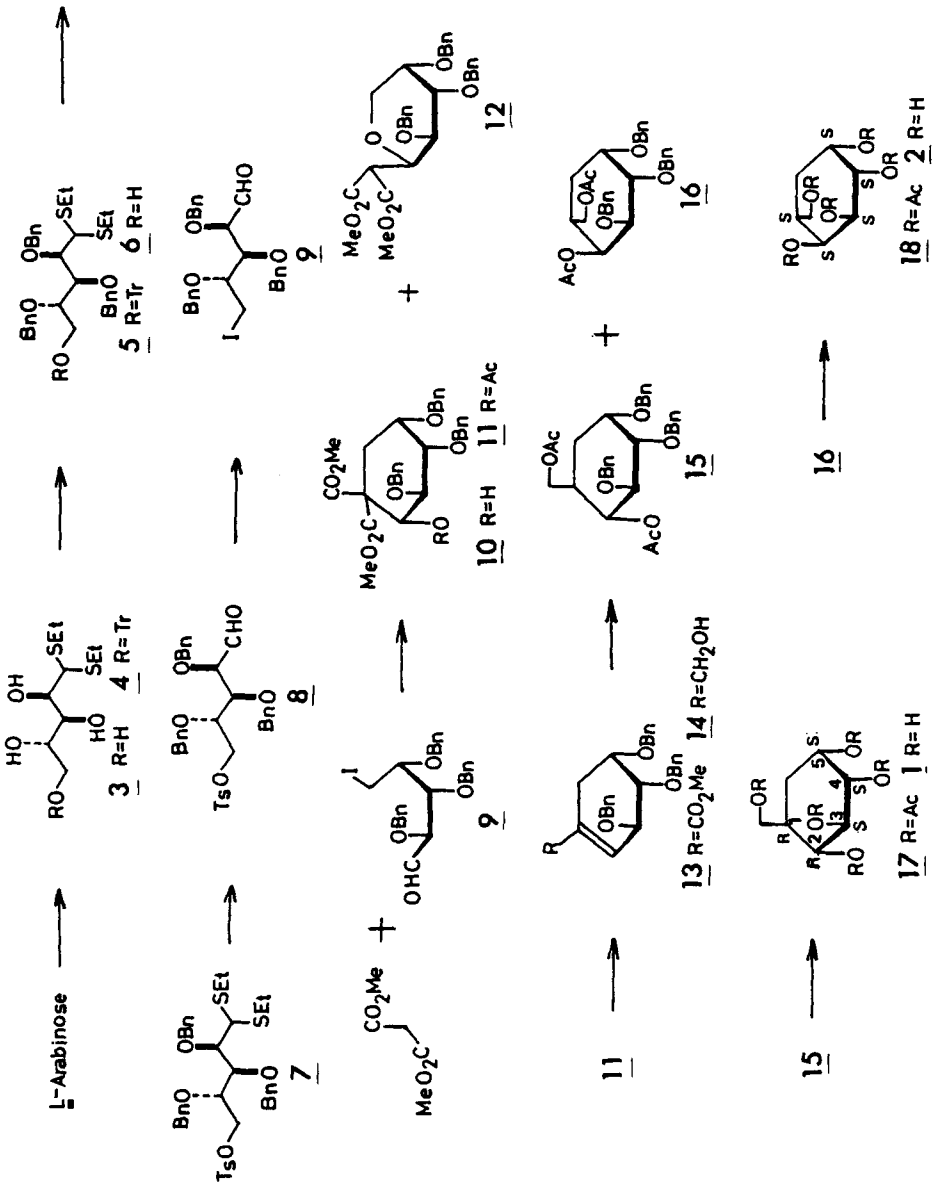
some antibiotics (validamycins) or as enzyme inhibitors, such as adiposins and amylostatins. Extensive synthetic approaches directed toward pseudo-sugars and related carbocyclic compounds have been reviewed by Ogawa recently.[1] Ogawa and Suami demonstrated the utility of 7-endo-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid, a Diels-Alder adduct of furan and acrylic acid, as a common starting material for pseudo-sugars synthesis.[1] They also succeeded in obtaining an excess of the optically active Diels-Alder adduct by an optical resolution technique, from which pseudo-α-D-galactopyranose and pseudo-β-D-glucopyranose were synthesized.[2] Paulsen and collaborators synthesized pseudo-α-D-galactopyranose and pseudo-β-D-mannopyranose from quebrachitol (2-O-methyl-L-chiroinositol) as an optically pure starting material.[3]



From our independent synthetic studies on optically active pseudo-sugars starting from carbohydrates,[4,5] we wish to describe herein syntheses of pseudo-α-D-glucopyranose (1) and pseudo-β-L-altropyranose (2) from L-arabinose.[6] The special worth of the present work is a one-step construction of suitably protected 2,3,4,5-tetrahydroxycyclohexane-1,1-dicarboxylate 11 by simultaneous C-C bond formation of an acyclic synthon 9 derived from L-arabinose with dimethyl malonate in the presence of sodium hydride. This compound (11) was then converted to the desired pseudo-sugars 1 and 2 through a cyclohexene derivative 13.

## RESULTS AND DISCUSSION

L-Arabinose diethyl dithioacetal (3), which was prepared by the resported procedure,[7] was preferentially tritylated with trityl chloride providing the 5-O-trityl derivative 4 in 89% yield. The secondary hydroxyl groups in 4 were then benzylated with benzyl bromide in the presence of sodium hydride to afford the tri-O-benzyl derivative 5. Removal of the trityl group in 5 by hydrolysis with p-toluenesulfonic acid gave O-detrityl derivative



6 in 61% yield from 4. O-Tosylation of 6 with p-toluenesulfonyl chloride in pyridine in the presence of 4-dimethylaminopyridine (DMAP) afforded the 5-O-tosyl derivative 7, which was subjected to the next step without purification.[8] Dethioacetalization of 7 with mercury(II) chloride and calcium carbonate in aqueous acetonitrile regenerated an aldehyde group to give 8.[8] Treatment of 8 with sodium iodide in refluxing 2-butanone afforded the synthon 9 as crystals in 50% yield from 6. The synthon 9 possesses two electrophilic sites at both terminal carbons. The crucial simultaneous C-C bond formation at both terminal carbons of 9 by attack of the methylene carbon of dimethyl malonate was next investigated. By stirring a THF solution of 9 with an excess of sodio dimethyl malonate, prepared by addition of sodium hydride to a THF solution of dimethyl malonate at ambient temperature, two products 10 and 12 were formed. The mixture could be separated after acetylation. Although acetylation of 10 afforded the cyclohexane derivative 11, the other product (12) was not acetylated. The mixture 11 and 12 were separated by silica gel chromatography, and the yield of the diastereomerically pure cyclohexane-1,1-dicarboxylate 11 was 43% (the C-glycosidic compound 12 was obtained in 33% yield). The structure of 11 was established by the $^1$H NMR spectrum, with an equatorial acetoxyl signal appearing at $\delta$ 1.99. Therefore, the configuration of the carbon bearing the newly introduced acetoxyl group in 11 was (R). The configuration of C-2 in 12 was deduced taking into consideration that 10 and 12 were formed via the common aldol adduct possessing R configuration on the carbon bearing hydroxyl group.

The transformation of 11 to the pseudo-sugars 1 and 2 was achieved by the following reaction sequence. Thermal demethoxycarbonylation of 11 by heating an aqueous DMSO solution of 11 containing NaCl at 110 to 170 $^{\circ}$C provided cyclohexene-1-carboxylate 13 in 75% yield as a result of successive $\beta$-elimination of the acetoxyl group. Lithium aluminium hydride ($LiAlH_4$) reduction of 13 gave an allyl alcohol 14 in 83% yield. Hydro-

boration of 14 with borane-THF complex at ambient temperature, and successive treatment with 35% aqueous $H_2O_2$ followed by acetylation furnished two fully protected pseudo-hexopyranoses 15 and 16, which were separated by silica gel chromatography, in 34% and 39% yield, respectively. The hydroboration proceeded non-stereoselectively. The structural establishment of the two pseudo-sugars 15 and 16 was achieved as follows. Treatment of 15 with sodium in liquid ammonia for removal of the protecting groups and successive acetylation afforded pentaacetate (17) of pseudo-α-D-glucopyranose in 49% yield. Similarly, the compound 16 was converted to pentaacetate (18) of pseudo-β-L-altropyranose in 38% yield. The $^1$H NMR spectrum of 17 was superimposable on that of the known DL-17, which was synthesized by Ogawa et al.[9] Likewise, comparison of the $^1$H NMR spectrum of 18 with that of the known DL-18[10] established the structure of 18 unambiguously. Finally, deprotection of 17 and 18 with sodium methoxide in methanol and successive purification by ion exchange resin gave rise to the free pseudo-sugars 1 and 2 in 65% and 86% yield, respectively.



## EXPERIMENTAL

General Procedures. Reactions were carried out at ambient temperature unless otherwise stated. Solutions were concentrated under diminished pressure below 40 °C (bath temperature). Melting points were determined with a Mitamura Riken micro mp apparatus and are uncorrected. Specific rotations were measured in a 1-dm tube with a Jasco DIP-4 polarimeter. Column chromatography was performed with Wakogel C-300 (Wako Pure Chemicals). TLC was carried out on glass plates coated with Wakogel B-5F, compounds being detected with UV light, and spraying with sulfuric acid followed by heating. IR spectra were recorded with a Hitachi Model-225 spectrometer (KBr) and with a Jasco Model A-202 spectrometer ($CHCl_3$). $^1$H NMR spectra

were recorded with a Varian EM-390 spectrometer, and chemical shifts for a $CDCl_3$ solution are recorded in δ values from internal tetramethylsilane. High resolution mass spectra were taken on a Hitachi M-80 mass spectrometer.

Dimethylformamide (DMF) was distilled over $CaH_2$ and then distilled. Pyridine was distilled over NaOH. Tetrahydrofuran (THF) was distilled over $LiAlH_4$ and then over sodium-benzoquinone.

5-O-Trityl-L-arabinose Diethyl Dithioacetal (4). To a solution of L-arabinose diethyl dithioacetal (3)[7] (4.83 g, 18.9 mmol) in pyridine (100 mL) were added trityl chloride (6.86 g, 24.6 mmol) and DMAP (461 mg, 3.8 mmol). The mixture was heated at 70 °C with stirring for 18 h and concentrated. The residue was partitioned between dichloromethane (300 mL) and water (300 mL), and the aqueous layer was extracted with dichloromethane (300 mL x 2). The combined organic layers were dried over $Na_2SO_4$ and concentrated. The residue was chromatographed on $SiO_2$ (250 g, ethyl acetate:toluene=1:20 containing 5% triethylamine), and fractions corresponding to $R_f$ 0.75 (ethyl acetate:toluene=1:1) were concentrated to afford 4 (8.45 g, 89%) as a pale yellow syrup. 4: $[\alpha]_D^{26}$+26.3° (c 1.33, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3540, 3440, 3020, 1490, 1450, 1210, 1080 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.25 (6H, t, J=8 Hz, 2 x $SCH_2\underline{CH_3}$), 2.66, 2.68 (2H x 2, each q, J=8 Hz, 2 x $S\underline{CH_2}CH_3$), 3.31 (2H, d, J=7 Hz, H-5,5'), 3.64-4.25 (4H, m, H-1,2,3,4), 7.20-7.70 (15H, m, $C(C_6H_5)_3$).

Anal. Calcd for $C_{28}H_{34}O_4S_2$: C, 67.45; H, 6.82; S, 12.86. Found: C, 67.36; H, 6.78; S, 12.56.

2,3,4-Tri-O-benzyl-L-arabinose Diethyl Dithioacetal (6). To a suspension of sodium hydride (60% emulsion in mineral oil, 3.30 g, 82.5 mmol, washed with hexane, 3 mL x 3, then dried) in DMF (5 mL) was added a DMF (75 mL) solution of 4 (8.25 g, 16.5 mmol). After stirring for 10 min, benzyl bromide (9.8 mL, 82.5 mmol) was added. The mixture was stirred for 32 h and ethanol (20 mL) was added, then evaporated. The residue was partitioned between ethyl acetate (400 mL) and water (400 mL), and the

aqueous layer was extratced with ethyl acetate (400 mL x 2). The combined organic layers were dried over $Na_2SO_4$ and concentrated to afford crude 5: $^1$H NMR ($CDCl_3$) δ 1.15 (6H, t, J=8 Hz, 2 x $SCH_2\underline{CH_3}$), 2.61 (4H, q, J=8 Hz, 2 x $S\underline{CH_2}CH_3$), 3.30 (1H, d, J=5 Hz, H-1), 3.65 (1H, dd, J=5 and 10 Hz, H-2), 4.44 (1H, d, J=7 Hz, H-4), 4.51-4.61 (2H, m, H-5,5'), 4.66 (6H, s, 3 x $O\underline{CH_2}C_6H_5$), 7.14-7.54 (30H, m, $C(C_6H_5)_3$, 3 x $OCH_2C_6\underline{H_5}$).

To a solution of the crude 5 in a mixture of ethyl acetate (40 mL) and methanol (40 mL) was added p-toluenesulfonic acid monohydrate (6.27 g, 33.0 mmol). The mixture was stirred for 2 days and neutralized by addition of saturated aqueous $NaHCO_3$, then concentrated. The residue was partitioned between dichloromethane (300 mL) and water (300 mL), and the aqueous layer was extracted with dichloromethane (300 mL x 2). The combined organic layers were dried over $Na_2SO_4$ and concentrated. The residue was chromatographed on $SiO_2$ (ethyl acetate:hexane= 1:20), and fractions corresponding to $R_f$ 0.57 (ethyl acetate: toluene=1:5) were concentrated to afford 6 (5.30 g, 61%) as a colorless syrup. 6: $[\alpha]_D^{20}$ -9.7° (c 1.14, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3010, 1450, 1200, 1080 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.20 (6H, t, J= 8 Hz, 2 x $SCH_2\underline{CH_3}$), 1.96-2.30 (1H, br s, OH), 2.63 (4H, q, J= 8 Hz, 2 x $S\underline{CH_2}CH_3$), 3.51-4.22 (6H, H-1,2,3,4,5,5'), 4.56-4.80 (6H, m, 3 x $O\underline{CH_2}C_6H_5$), 7.38 (15H, s, 3 x $OCH_2C_6\underline{H_5}$). High resolution mass spectrum, calcd for $C_{30}H_{38}O_4S_2$: m/z M, 526.2208, found: M, 526.2189.

2,3,4-Tri-O-benzyl-5-deoxy-5-iodo-aldehyde-L-arabinose (9). To a solution of 6 (5.83 g, 11.1 mmol) in pyridine (30 mL) were added p-tosyl chloride (12.7 g, 66.6 mmol) and DMAP (542 mg, 4.4 mmol). The mixture was stirred for 18 h and concentrated. The residue was partitioned between dichloromethane (200 mL) and water (200 mL), and the aqueous layer was extracted with dichloromethane (200 mL x 2). The combined organic layers were dried over $Na_2SO_4$ and concentrated to afford crude 7 ($R_f$ 0.39; ethyl acetate:hexane=1:5): $^1$H NMR ($CDCl_3$) δ 1.16 (6H, t, J=8 Hz, 2 x $SCH_2\underline{CH_3}$), 2.37 (3H, s, $OSO_2C_6H_4\underline{CH_3}$), 2.56, 2.65 (2H x 2, each

q, J=8 Hz, 2 x $SC\underline{H}_2CH_3$), 3.76-4.32 (6H, m, H-1,2,3,4,5,5'), 4.49-4.71 (6H, m, 3 x $OC\underline{H}_2C_6H_5$), 7.10-7.50 (15H, m, 3 x $OCH_2C_6\underline{H}_5$), 7.68-7.88 (4H, m, $OSO_2C_6\underline{H}_4CH_3$).

To a solution of the crude 7 in a mixture of acetonitrile (50 mL) and water (10 mL) were added mercury(II) chloride (12.0 g, 44.3 mmol) and calcium carbonate (5.00 g, 50.0 mmol). The mixture was stirred for 2 h, and the resulting insoluble solids were removed by filtration. The filtrate was concentrated, the residue was dissolved in dichloromethane (150 mL) and washed with 1 M aqueous KI solution (150 mL x 3). The organic layer was concentrated to afford crude 8 ($R_f$ 0.40; ethyl acetate:hexane=1:3); $^1$H NMR ($CDCl_3$) δ 2.38 (3H, s, $OSO_2C_6H_4C\underline{H}_3$), 3.70-4.24 (5H, m, H-2,3,4,5,5'), 4.34-4.54 (6H, m, 3 x $OC\underline{H}_2C_6H_5$), 7.31 (15H, s, 3 x $OCH_2C_6\underline{H}_5$), 7.77 (4H, ABq, $OSO_2C_6\underline{H}_4CH_3$), 9.64 (1H, s, CHO).

A solution of the crude 8 in dry 2-butanone (dried over $CaCO_3$ and distilled, 30 mL) containing sodium iodide (8.30 g, 55.3 mmol) was refluxed for 18 h in the dark. The mixture was concentrated, the residue was partitioned between ethyl acetate (200 mL) and water (200 mL), and the aqueous layer was extracted with ethyl acetate (200 mL x 2). The organic layers were washed with 30% aqueous $Na_2S_2O_3$ solution (200 mL x 2), dried over $Na_2SO_4$ and concentrated. The residue was chromatographed on $SiO_2$ (500 g, ethyl acetate:hexane=1:20), and fractions corresponding to $R_f$ 0.48 (ethyl acetate:hexane=1:5) were concentrated to afford 9 (2.94 g, 50%), mp 55-56 °C: $[\alpha]_D^{17}$ +8.7° (c 1.22, $CHCl_3$); IR $\nu_{max}^{KBr}$ 3010, 1730, 1200, 1080 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ 3.23-4.21 (5H, m, H-2,3,4,5,5'), 4.52-4.61 (6H, m, 3 x $OC\underline{H}_2C_6H_5$), 7.33 (15H, s, 3 x $OCH_2C_6\underline{H}_5$), 9.64 (1H, s, CHO).

Anal. Calcd for $C_{26}H_{27}IO_4$: C, 58.88; H, 5.13; I, 23.92. Found: C, 58.90; H, 5.09; I, 23.71.

Reaction of Compound 9 with Dimethyl Malonate in the Presence of Sodium Hydride. Dimethyl (2R,3S,4S,5S)-2-Acetoxy-3,4,5-tris(benzyloxy)cyclohexane-1,1-dicarboxylate (11) and

(2R,3S,4S,5S)-3,4,5-Tris(benzyloxy)-2-[(bismethoxycarbonyl)-methyl]tetrahydropyran (12). The reaction was carried out under argon atmosphere. To a stirred suspension of sodium hydride (60%, 219 mg, 5.48 mmol, washed with hexane then dried) in THF (18 mL) was added dimethyl malonate (0.62 mL, 5.48 mmol). After stirring for 10 min, a solution of 9 (968 mg, 1.83 mmol) in THF (10 ml) was added. The mixture was stirred for 3 h and ethanol (0.1 mL) was added. The mixture was diluted with water (100 mL) and extracted with ethyl acetate (100 mL x 3). The combined extracts were dried over $Na_2SO_4$ and concentrated to afford a crude mixture of 10 and 12, which was acetylated without separation [TLC (ethyl acetate:hexane=1:3), 10: $R_f$ 0.30, 12: $R_f$ 0.28]. The mixture was acetylated with acetic anhydride (8 mL) in pyridine (8 mL) in the presence of DMAP (105 mg) for 18 h. After concentration of the mixture, the residue was chromatographed on $SiO_2$ (100 g, ethyl acetate:hexane=1:7). Fractions corresponding to $R_f$ 0.38 (ethyl acetate:hexane=1:3) were concentrated to afford 11 (454 mg, 43%) as crystals, and fractions corresponding to $R_f$ 0.28 were concentrated to afford 12 (324 mg, 33%) as a colorless syrup. 11: mp 76-77 °C; $[\alpha]_D^{19}$ +10.7° (c 1.12, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3100-2800, 1775, 1740, 1495, 1450, 1435, 1370, 1260, 1220 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.99 (3H, s, $OCOCH_3$), 2.18-2.85 (2H, m, H-6,6'), 3.32-4.91 (9H, m, H-3,4, 5, 3 x $OCH_2C_6H_5$), 3.45, 3.65 (3H x 2, each s, 2 x $COOCH_3$), 6.18-6.28 (1H, br d, H-2), 7.30 (15H, s, 3 x $OCH_2C_6H_5$).

Anal. Calcd for $C_{33}H_{36}O_9$: C, 68.73; H, 6.29. Found: C, 68.87; H, 6.38.

12: $[\alpha]_D^{19}$+7.7° (c 0.65, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3100-2850, 1755, 1740, 1495, 1450, 1435, 1320, 1250 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 3.25-4.22 (6H, m, H-2,3,4,5,6,6'), 3.54, 3.69 (3H x 2, each s, 2 x $COOCH_3$), 4.50-4.72 (6H, m, 3 x $OCH_2C_6H_5$), 5.02 (1H, d, J=12 Hz, $CH(COOCH_3)_2$), 7.31 (15H, s, 3 x $OCH_2C_6H_5$). High resolution mass spectrum, calcd for $C_{31}H_{33}O_8$: m/z M-H, 533.2172, found: M-H, 533.2171.

Methyl (3S,4S,5S)-3,4,5-Tris(benzyloxy)-1-cyclohexene-1-carboxylate (13). A solution of 11 (413 mg, 0.72 mmol) in a mixture of DMSO (12 mL) and water (0.5 mL) containing NaCl (167 mg) was heated from 110 to 170 °C for 3 h with stirring. After heating at 170 °C more 1 h, the mixture was cooled to ambient temperature. The solution was diluted with ethyl acetate (50 mL), washed with water (50 mL x 3). The organic layer was dried over $Na_2SO_4$ and concentrated. The residue was chromatographed on $SiO_2$ (100 g, ethyl acetate:hexane=1:12), and fractions corresponding to $R_f$ 0.39 (ethyl acetate:hexane=1:4) were concentrated to afford 13 (247 mg, 75%) as a colorless syrup. 13: $[\alpha]_D^{17}$+63.8° (c 0.85, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3100-2800, 1720, 1650, 1495, 1450, 1430, 1360, 1240 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 2.51-2.70 (2H, m, H-6,6'), 3.72 (3H, s, $COOCH_3$), 3.74-4.41 (3H, m, H-3,4, 5), 4.63-4.68 (6H, m, 3 x $OCH_2C_6H_5$), 6.80-6.94 (1H, m, H-2), 7.35 (15H, s, 3 x $OCH_2C_6H_5$). High resolution mass spectrum, calcd for $C_{29}H_{30}O_5$: m/z M, 458.2091, found: M, 458.2100.

(3S,4S,5S)-3,4,5-Tris(benzyloxy)-1-hydroxymethyl-1-cyclohexene (14). To a stirred solution of 13 (234 mg, 0.51 mmol) in THF (5 mL) was added a suspension of $LiAlH_4$ (31 mg, 0.82 mmol) in THF (3 mL) at -15 °C. The mixture was stirred for 1 h at that temperature, and ethyl acetate (0.1 mL) was added. The resulting insoluble solids were removed by filtration, and the filtrate was concentrated. The residue was chromatographed on $SiO_2$ (20 g, ethyl acetate:toluene=1:7), and fractions corresponding to $R_f$ 0.13 (ethyl acetate:toluene=1:10) were concentrated to afford 14 (181 mg, 83%) as a colorless syrup. 14: $[\alpha]_D^{20}$+65.8° (c 0.76, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3450, 3080, 3050, 2990, 2850, 1500, 1450, 1370, 1350, 1260, 1200 $cm^{-1}$; $^1H$ NMR δ 2.19-2.45 (2H, m, H-6,6'), 3.62-4.80 (12H, m, H-3,4,5, $CH_2OH$, 3 x $OCH_2C_6H_5$), 5.52-5.77 (1H, m, H-2), 7.35 (15H, s, 3 x $OCH_2C_6H_5$). High resolution mass spectrum, calcd for $C_{28}H_{30}O_4$: m/z M, 430.2141, found: M, 430.2130.

Hydroboration of Compound 14 and Successive Oxidative Treatment with $H_2O_2$. (1R,2R,3S,4S,5S)- (15) and (1S,2S,3S,4S, 5S)- (16) 2-Acetoxy-1-acetoxymethyl-3,4,5-tris(benzyloxy)cyclo-

hexane. The reaction was carried out under argon atmosphere. To a stirred solution of 14 (542 mg, 1.26 mmol) in THF (15 mL) was added borane-THF complex (1 M in THF, 12.6 mL, 12.6 mmol) at 0 °C, then the mixture was stirred at ambient temperature for 1 h. To the mixture was added water (2.8 mL), 3 M aqueous NaOH solution (4.1 mL), and 35% aqueous $H_2O_2$ (4.3 mL), successively. The mixture was stirred for 3 h and concentrated. The residue was partitioned between ethyl acetate (50 mL) and water (50 mL), and the aqueous layer was extracted with ethyl acetate (50 mL x 2). The combined organic layers were dried over $Na_2SO_4$ and concentrated. The residue was acetylated with acetic anhydride (10 mL) in pyridine (10 mL) for 18 h. After removal of the reagents, the residue was chromatographed on $SiO_2$ (50 g, ethyl acetate:toluene=1:12). Fractions corresponding to $R_f$ 0.78 (ethyl acetate:toluene=1:2) were concentrated to afford 16 (263 mg, 39%) as a colorless syrup, and fractions corresponding to $R_f$ 0.67 were concentrated to afford 15 (240 mg, 34%) as crystals.
15: mp 98-100 °C; $[\alpha]_D^{21}$+20.0° (c 1.25, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3020, 1740, 1360, 1030 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.77-2.09 (3H, m, H-1,6, 6'), 1.90, 1.99 (3H x 2, each s, 2 x $OCOCH_3$), 3.21-5.06 (12H, m, H-2,3,4,5, $CH_2OAc$, 3 x $OCH_2C_6H_5$), 7.30, 7.35 (15H, each s, 3 x $OCH_2C_6H_5$). High resolution mass spectrum, calcd for $C_{32}H_{36}O_7$: m/z M, 532.2458, found: M, 532.2454.
16: $[\alpha]_D^{20}$-23.9° (c 0.67, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3020, 1730, 1370, 1210, 1030 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.70-2.08 (3H, m, H-1,6,6'), 2.00, 2.02 (3H x 2, each s, 2 x $OCOCH_3$), 3.60-5.20 (12H, m, H-2, 3,4,5, $CH_2OAc$, 3 x $OCH_2C_6H_5$), 7.32 (15H, s, 3 x $OCH_2C_6H_5$). High resolution mass spectrum, calcd for $C_{32}H_{37}O_7$: m/z M+H, 533.2536, found: M+H, 533.2505.

(1R,2R,3S,4S,5S)-2,3,4,5-Tetraacetoxy-1-(acetoxymethyl)-cyclohexane, Pseudo-α-D-glucopyranose Pentaacetate (17). Sodium (90 mg, 3.9 mmol) was dissolved in liquid ammonia (30 mL) at -78 °C. To the solution was added a THF (3 mL) solution of 15 (123 mg, 0.23 mmol). After 10 min, sodium (90 mg) was added. The mixture was kept for 1 h at -78 °C, then ammonium chloride

(40 mg) was added. After warming to ambient temperature, the solution was concentrated. The residue was acetylated with acetic anhydride (4 mL) in pyridine (4 mL) for 18 h. After removal of the reagents, the residue was chromatographed on $SiO_2$ (20 g, ethyl acetate:toluene=1:5). Fractions corresponding to $R_f$ 0.47 (ethyl acetate:hexane=1:2) were concentrated to afford 17 (42 mg, 47%) as a colorless syrup. 17: $[\alpha]_D^{22}$+36.7° (c 0.79, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3020, 1740, 1370, 1220, 1050 $cm^{-1}$. The $^1H$ NMR spectrum of 17 was superimposable on that of the DL-17.[9] High resolution mass spectrum, calcd for $C_{17}H_{25}O_{10}$: M+H, 389.1445, found: M+H, 389.1422.

(1S,2S,3S,4S,5S)-2,3,4,5-Tetraacetoxy-1-(acetoxymethyl)-cyclohexane, Pseudo-β-L-altropyranose Pentaacetate (18). By analogous conditions and work-up as described above, compound 16 (159 mg) was converted to 18 (46 mg, 38%) after $SiO_2$ chromatography (ethyl acetate:toluene=1:5). Compound 18 was obtained as a colorless syrup: $R_f$ 0.49 (ethyl acetate:toluene=1:2); $[\alpha]_D^{21}$+6.7° (c 0.75, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3020, 1740, 1370, 1230, 1050 $cm^{-1}$. The $^1H$ NMR spectrum of 18 was superimposable on that of the DL-18.[10] High resolution mass spectrum, calcd for $C_{17}H_{25}O_{10}$: m/z M+H, 389.1446, found: M+H, 389.1448.

(1R,2R,3S,4S,5S)-2,3,4,5-Tetrahydroxy-1-(hydroxymethyl)-cyclohexane, Pseudo-α-D-glucopyranose (1). To a solution of 17 (86 mg, 0.22 mmol) in methanol (2 mL) was added sodium methoxide in methanol (1 M, 1.5 mL, 1.5 mmol), and the mixture was stirred for 3 h. The solution was neutralized by addition of Amberlite 120 ($H^+$), and the resin was removed by filtration. After concentration of the filtrate, the residue was dissolved in methanol (2 mL) and decolorized with active carbon at 60 °C. After removal of the carbon, the filtrate was concentrated to afford 1 (25 mg, 65%) as a colorless syrup. 1: TLC $R_f$ 0.27 (chloroform:methanol=3:1); $[\alpha]_D^{25}$+30.0° (c 1.00, $CH_3OH$). High resolution mass spectrum, calcd for $C_7H_{15}O_5$: m/z M+H, 179.0919, found: M+H, 179.0930.

(1S,2S,3S,4S,5S)-2,3,4,5-Tetrahydroxy-1-(hydroxymethyl)-cyclohexane, Pseudo-β-L-altropyranose (2). The compound 18 (110 mg) was O-deacetylated as described in preparation of 1 providing 2 (43 mg, 86%) as a colorless syrup. 2: TLC $R_f$ 0.40 (chloroform:methanol=3:1); $[\alpha]_D^{24}$ -49.5° (c 1.03, $CH_3OH$). High resolution mass spectrum, calcd for $C_7H_{15}O_5$: m/z M+H, 179.0921, found: M+H, 179.0927.

ACKNOWLEDGEMENT

The authors are grateful to Professor Seiichiro Ogawa (Keio University) for his useful discussion on the structural determination of the synthesized pseudo-sugars described in the present work. Elemental analyses were performed by Mr. Saburo Nakada (Keio University) whom the authors also thank.



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